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COMPLETE SPECIFICATION

Sheet Material of Fibrous Cellulose and Glass Fibrous Rovings

We, HAWLEY PRODUCTS COMPANY, a Corporation organized and existing under the Laws of the State of Delaware, United States of America, whose post office address is St. Charles, State of Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to sheet material containing glass fibres and to a method for the manufacture thereof.

It has heretofore been sngested that glass fibres can be incorporated into paper during the process of making the paper and weak glass papers have been produced. However, as a practical matter it is very difficult to incorporate glass fibres into paper and produce a satisfactory product of improved strength.

One of the objects of this invention is to provide a new and improved method for incorporating glass fibres with cellulose on a paper making machine.

A further object is to provide a new and improved process for incorporating glass fibres with cellulose which results in sheet materials that are free from the disadvantages heretofore attending the use of glass fibres in paper. Other objects will appear hereinafter.

In accomplishing these objects in accordance with this invention it has been found that glass fibres can be incorporated with cellulose prior to the formation of a sheet and on a paper making machine by adding them in the form of rovings or bundles of glass filaments cut into lengths from about 1/8 inch to 6 inches, preferably around 1/2 inch. The glass fibre rovings of commerce are suitable for the purpose of the invention. These are ordinarily made from glass filaments of approximately 0.00038 inch in diameter. About 102 to 204 of such filaments are collected in a bundle. A roving consists of about 60 such bundles. For the purpose of the present invention the roving or the bundles should be coated with a substance that imparts an affinity for resins to glass, as, for example, stearato chromyl chloride, vinyl trichlorosilane and materials of the type disclosed in U.S. Patents Nos. 2,273,040, 2,359,858, 2,381,752 and 2,401,645. It is known in the art to coat glass rovings or bundles of filaments with such materials.

When glass rovings are cut and placed in water they tend to fall apart and produce an unmanageable mass of very fine individual glass filaments. This is true even though they are coated with coating materials of the type previously described that increase their affinity for resins. The tendency to fall apart is greatly accelerated if the glass rovings are beaten in paper and pulp handling apparatus.

We have found that this tendency of the cut glass bundles to disintegrate into individual filaments in water can be overcome by adding to the water prior to the addition of the cut glass rovings an uncured resin having an affinity for the glass, preferably a polyester resin. The resin can be added simultaneously or contemporaneously with the cut glass rovings but if it is added too long after the glass the desired result cannot be obtained because the glass fibres will tend to fall apart before they become coated with the resin.

In the preferred practice of the invention a slurry is prepared containing cellulose fibres, cut glass rovings are pre-wet with water insufficiently to cause the glass fibres to separate and a polyester resin is added to the slurry of cellulose fibres. Resins of this type do not appear to have an affinity for cellulose fibres and hence do not coat the cellulose fibres substantially. The pre-wet cut glass rovings are then added to the resin

mixture and stirred therewith over a limited period of time, preferably one to ten minutes, or until the resin coats the glass fibres. The coating of the glass fibres by the resin occurs almost immediately and is evidenced from the fact that the oily appearance of the mixture disappears. The resultant mixture is then ready to be processed into sheet materal.

If the sheet material is being manufactured on a Fourdrinier paper making machine the cellulose-uncured resin-cut glass roving mixture in water is added to the head box of the machine or at some other point prior to the formation of the sheet where it is not subjected to severe agitation. In a cylinder paper making machine the mixture containing the glass fibres coated with uncured resin is added in the vat of the cylinder machine.

During the formation of the sheet material either on the cylinder machine or on the Fourdrinier machine the glass fibres will become integrated with the cellulose and a satisfactory paper product containing glass fibres is obtained.

The characteristics of the sheet material can be varied depending upon the quantity of the glass fibre material which is added thereto. A definite improvement in tear strength is obtained with the addition of 5% of glass fibres based on the dry weight of the sheet material. In general, for making bag papers it is preferable to incorporate a sufficient quantity of the resin-glass material into the paper mix to produce a paper product containing 5% to 30% by weight of glass fibres calculated on the dry weight of the paper. For specific types of paper up to 80% or 90% glas fibres can be added, e.g., for a sheet to be subsequently saturated with resin and moulded.

The function of the resin is to hold the glass filaments together in thread-like glass bundles until the sheet has been formed. The properties of the sheet material can also be varied depending upon the quantity of the resin used whether a flexible or rigid type is selected, and upon whether a catalyst is incorporated with the resin. The drying of the sheet as is customary in paper making processes will have a curing affect upon the polyester resins and other types of heat setting resins. The extent to which this curing occurs can be increased by adding a catalyst to the resin. Where a relatively stiff sheet is desired the curing of the resin coating the fibre will have a beneficial effect in producing this result because it tends to stiffen the cut glass bundles on which the resin is coated. On the other hand, where a more pliable or flexible sheet is desired the process should be carried out with as little curing of the resin as is possible, and with a flexible type polyester.

The resin additions heretofore mentioned function principally to hold the glass filaments together in thread-like bundles of cut filaments. In order to obtain sheet material improved strength from the glass, it is necessary to firmly bind the protected glass fibre in the sheet. This necessitates the use of

(a) highly beaten cellulose and/or
(b) resin addition to the cellulose in the beater and/or
(c) tub sizing and/or subsequent resin impregnation of the paper, after it is off the machine.

In addition to these treatments to bind the glass into the sheet it may be desired to incorporate other treatments, such as a wet strength resin, water repellant sizing, and the like.

If a sheet material is desired in which the glass is bound, a very effective way of accomplishing this result is to add another resin such as a urea-formaldehyde resin or a melamine formaldehyde resin to the mixture in the beater, or at least ahead of the points of addition of the resin containing cut glass rovings. As an illustration, the addition of 2% to 5% by weight of the sheet material of a melamine-formaldehyde resin in the beater will produce a sheet material to which the uncured resin-cut glass rovings can be added with very satisfactory results. Rubber, polyvinyl acetate or other thermoplastic resins can be added.

The invention will be illustrated but is not limited by the following examples in which the quantities are stated in parts by weight unless otherwise indicated.

EXAMPLE I

Twenty (20) pounds of Kraft pulp previously beaten to a Williams freeness of 20 seconds are dispersed in 150 gallons of water. Five (5) pounds of an uncured liquid polyester heat setting resin are poured into the tank containing the slurry of Kraft fibres and mixed therewith at a temperature of 120°F. Immediately thereafter 50 pounds of 1/4 to 1/2 inch cut glass fibre rovings pre-coated with a substance which produces an affinity for polyester resins which have been pre-wet with water so that they will sink more quickly are added to the resin-Kraft mixture and mixing is effected for about 3 or 4 minutes. Air agitation is usually employed during this mixing.

The resultant composition is then flowed into the head box of a Fourdrinier paper making machine. The quantities added are varied to a glass fibre content of 5% to 30% based on the dry weight of the sheet material.

The water is preferably heated to the temperature mentioned so that the viscosity of the resin will remain low enough to permit the resin to distribute itself and to give it time to penetrate the glass fibre bundles.

The temperature of heating at this mixing stage should preferably be below the temperature at which the resin cures, otherwise the glass fibres will be stiffened by the resin and may interfere with the sheet formation.

EXAMPLE II

The procedure employed is the same as that described in Example I except that the mixture prepared as described in Example I is added to the vat of a cylinder paper making machine instead of to the head box of a Fourdrinier paper making machine.

EXAMPLE III

The procedure is the same as in Example II except that the resin-cut glass composition is added to the middle cylinder of a three-cylinder paper making machine whereby a three-ply paper is obtained in which the middle or intermediate ply contains glass fibres.

EXAMPLE IV

Twenty (20) pounds of refined rag beaten to a freeness of 25 on the Williams scale are dispersed in 150 gallons of water at a temperature of 120°F. Five (5) pounds of a thermosetting uncured liquid flexible-type polyester catalyzed with 1% benzoyl peroxide are poured into the tank and immediately 5 pounds of 1-inch cut glass fibre rovings pre-coated with a substance which produces an affinity for polyester resins are added. Good agitation is applied during the process, some of which may be from air injection.

The temperature of the slurry is now raised to 180°F. to 200°F. and held there until a test shows the resin on the fibre to be thermoset. The mass may now be dewatered for storage or used directly.

A bleached and beaten Kraft pulp is now prepared containing 25 parts by weight polyvinyl acetate to 100 parts by weight of fibre and 2 parts by weight cationic melamine wet strength resin. This may be done using the so-called Bardac process in which the cationic melamine particle first affixes itself to the anionic cellulose fibre and the polyvinyl acetate emulsion particle then discharges and affixes itself thereon.

The rag-glass and Kraft-resin pulp is now combined in the desired ratio, e.g., to give 10% glass in the final sheet and run over the paper machine.

EXAMPLE V

The procedure was the same as in Example IV except that instead of adding resin to the cellulose fraction in the beater the rag-glass and Kraft sheet is run through phenolic resin at the size station at the middle of the drying section of the paper machine.

EXAMPLE VI

The procedure was the same as in Example IV except that an oil soluble colour is added to the polyester resin treating the glass to provide a pleasing pattern in the final sheet.

EXAMPLE VII

Example IV is run without curing the resin, e.g., the glass-resin is not heated beyond 120°F., and the polyester is cured while passing over the drying section of the paper machine. This allows the polyester resin to re-enforce the sheet binding resin.

EXAMPE VIII

The procedure is the same as in Example IV except that the catalyst is omitted so that the polyester resin is not cured when the paper is rolled up. This improves the pliability of the sheet.

EXAMPLE IX

The procedure is the same as in Example IV except that asbestos is substituted for 10% of the bleached Kraft.

The resins employed in the foregoing examples can be prepared in a number of different ways, for instance, a relatively flexible resin of the type which it is desirable to use in Examples I and II is prepared by condensing 2 mols of ethylene glycol, 1 mol of maleic anhydride and 1 mol of adipic acid for 3 hours at 160°C. under an atmosphere of carbon dioxide and to the resultant resin there is added 20% to 30% by weight of styrene and 1% by weight of benzoyl peroxide. This produces what may be described as a catalyzed polyester resin, the benzoyl peroxide being the catalyst. This resin is a heat setting resin and will cure at temperatures in the neighbourhood of 180°F. or higher.

A more rigid polyester resin can be obtained by omitting the adipic acid in the foregoing preparation and substituting 1 mol of maleic anhydride. The more rigid types of resins can suitably be employed in Example III where the resultant sheet material contains outer plies of cellulose that will prevent the glass fibres from protruding beyond the surface of the sheet.

In a similar manner other resins are prepared which are suitable for the practice of the invention. Instead of ethylene glycol, any of the normally liquid polyethylene glycols can be employed such as Polyethylene Glycol 200, Polyethylene Glycol 300 and Polyethylene Glycol 400 (polyethylene glycols having molecular weights of 200, 300 and 400 respectively). Instead of styrene, compounds capable of polymerizing such as diallyl phthalate, can be used.

The employment of a catalyst in the heat setting resins is optional.

The preferred resins employed for the purpose of the invention can be described as condensation products of a polyhydric alcohol and a polybasic acid (or the corresponding acid anhydride) and monomeric aryl compounds having a vinyl side chain. Usually at least a portion of the polybasic

acid component is maleic anhydride. The polyhydric alcohol-polybasic acid composition is added to 10% to 40% by weight of a monomeric aryl vinyl compound, such as styrene. For example, a relatively rigid or non-flexible resin can be prepared by reacting 2 mols of ethylene glycol with 1 mol of phthalic anhydride and 1 mol of maleic anhydride for 2 to 4 hours at a temperature of 160°C. in an inert atmosphere such as nitrogen, carbon dioxide or illuminating gas (a gas mixture containing approximately H (50%), CH_4 (28%), O_nH_{2n} (4.5%), CO (2%), N (2%), O (6%)) and then adding to the resultant product 10% to 40% monomeric styrene. The resin in this form is liquid and usually has an acid number around 10 to 50. When this liquid resin is heated with a curing catalyst a solid, infusible resin is formed.

Suitable catalysts are the organic peroxides which are soluble in the hydrophobe or resin phase, e.g., benzoyl peroxide, acetylbenzoyl peroxide, cumene hydroperoxide, para tertiary butyl perbenzoate, and other oil soluble oxygen supplying catalysts.

In order to produce flexible thermosetting polyester resins higher molecular weight polyalkylene glycols, e.g., polyethylene glycol 200, e.g., polyethylene glycol 400, polyoxypropylene glycols and mixed polyoxyethylene-polyoxypropylene glycols are substituted for the ethylene glycol, or a portion of the dibasic acid is adipic or higher number of carbon atoms.

Instead of styrene other monomeric aryl compounds having an unsaturated side chain can be employed, e.g., vinyl toluenes, vinyl naphthalenes, vinyl ethyl benzenes, alpha methyl styrene, vinyl chlorobenzenes, vinyl xylenes, divinyl benzene, divinyl toluenes, divinyl naphthalenes, divinyl xylenes, divinyl ethyl benzenes, divinyl chlorobenzenes, divinyl-phenyl vinyl ethers and diallyl pthalate. Lower boiling monomers such as vinyl acetate usually are not satisfactory because the reaction which takes place when the resin is cured is very exothermic and the heat would drive off low boiling monomers.

The cellulose fibres which are incorporated with the resin and the cut-glass rovings have the characteristic that they tend to spread the cut glass and keep it from agglomerating until the resin has an opportunity to penetrate the bundles of the glass fibres. The weight ratio of cellulose to glass is preferably within the range of 1:10 to 1:1 and especially good results have been obtained by using a ratio of cellulose to glass within the range of 1:5 to 3:5. The cellulose also assists in the proper felting of the glass and increases the wet strength of the formed felt. Examples of suitable cellulose fibres which can be employed for the purpose of the invention are envelope clippings, refined rag, Kraft, cotton linters, caroa, henequen and other cellulose fibres. Caroa fibre seems to have exceptional properties in keeping glass fibres separate while the resin is being put on the glass. Caroa is a Brazilian pineapple fibre and for the purpose of the invention is subjected to a hammer mill and bleaching operation before put in use.

The fusible resin which is added to the fibre during the wet processing should preferably have a viscosity within the range of 100 to 1,000 centipoises. However, resins having a greater viscosity can be used by diluting them with a solvent such as methylethyl ketone.

The quantity of the resin added should be at least 5% and not exceeding about 50% by weight of the fibres. Especially good results are obtained with about 10% to 20% resin based on the weight of the glass fibres. Too much resin causes grease spots and agglomeration of the glass fibres and too little does not hold the filaments together.

The consistency of the composition which is added to the paper making machine is preferably within the range of 0.1% to 6% by weight of fibre and in most cases it is desirable to use a consistency of about 0.2 to 0.3% of total fibre based on the weight of the water.

The invention makes it possible to incorporate glass fibres into sheet material while producing a product having satisfactory properties, including increased dimensional stability and tear strength. One of the principal advantages of the invention is that it makes it possible to maintain the fibre integrity of the glass fibres during processing and overcomes the difficulties heretofore experienced due to the glass fibres being unwrapped and forming unmanageable cottony masses and lumps. In the felted products herein described containing both cellulose fibres and cut bundles of glass rovings the cellulose fibres and the bundles of glass fibres are intermingled and distributed with respect to each other.

What we claim is:—

1. A wet felted sheet material consisting essentially of cellulose fibres and glass fibre rovings intermingled and distributed with respect to each other, the glass fibre rovings consisting of thread-like bundles of individual glass filaments pre-coated with a substance which produces an affinity for polyester resins, cut into lengths from about 1/8 inch to 6 inches and coated with about 5 to 50% by weight of a polyester resin having an affinity for the pre-coated glass fibres, and the glass fibres constituting 5% to 90% by weight of the total fibres, calculated on the dry weight of the fibres.

2. A method of making the sheet material of Claim 1, which comprises adding to water, glass fibre rovings cut into lengths

from about 1/8 inch to 6 inches to form a slurry, contemporaneously adding a thermosetting uncured polyester resin to said slurry, said rovings being coated with a substance which produces an affinity of said resin for the glass, the proportions of said resin being sufficient to bind said fibres together to prevent the rovings from disintegrating into individual filaments in said water, stirring the slurry until said resin coats said rovings, and adding the resultant slurry to a paper making composition including cellulose fibre at a point in the paper making process where the paper making composition is no longer subject to severe agitation and prior to the formation of the sheet material.

3. The method as claimed in Claim 2 wherein the slurry of the resin coated cut glass fibre rovings is added to the head box of a Fourdrinier paper making machine.

4. The method as claimed in Claim 2 wherein the slurry of the resin coated cut glass fibre rovings is added to the vat of a cylinder paper making machine.

5. A method of making the sheet material claimed in Claim 1 which comprises preparing a slurry in water containing cellulose fibres and a thermosetting uncured polyester resin which does not have an affinity for the cellulose fibres but has an affinity for glass fibres which have been treated to produce such affinity, adding glass fibre rovings treated with a substance to produce such affinity cut into lengths from about 1/8 inch to 6 inches to the slurry of cellulose fibres and resin in water, stirring the resultant mixture until the resin coats the glass fibres, diluting the resultant composition with water to a felting consistency, and felting a sheet from said composition.

6. The method as claimed in Claim 5 in which the quantity of resin is within the range of 5% to 50% by weight of the total fibre.

7. The method as claimed in Claim 5 in which the quantity of resin is within the range of 10% to 20% by weight of the glass fibres.

8. The method as claimed in Claim 5 in which the quantity of glass fibres is within the range of 5% to 30% by weight of the sheet.

9. A method of making the sheet material claimed in Claim 1 which comprises preparing an aqueous slurry of a cellulose paper pulp containing about 2% to 5% calculated on the dry weight of the paper of a resin, such as urea-formaldehyde or melamine-formaldehyde, which imparts wet strength to the paper, subsequently adding to said paper pulp an emulsion of a resin which breaks in the presence of said wet strength resin and affixes itself to the cellulose fibre, separately preparing an aqueous slurry of glass fibre rovings cut into lengths from about 1/8 inch to 6 inches and adding to cellulose fibres in water contemporaneously with a thermosetting uncured resin having an affinity for the glass fibres but substantially no affinity for the cellulose, combining the cellulose-resin slurry and the cellulose-glass slurry, diluting the resultant composition to a felting consistency, and felting the resultant product to a sheet.

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